A SEALED-CHAMBER METHOD FOR THE STUDY OF THE
RELATIVE AFFINITY OF OXIDE MELTS FOR TRACE MOLYBDENUM
AND CESIUM VAPOR SPECIES AT 1100-1300°C

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**A SEALED-CHAMBER METHOD FOR THE STUDY OF THE RELATIVE AFFINITY
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A B S T R A C T

Molten oxide droplets containing various proportions of Na_2O , CaO , Fe_2O_3 , Al_2O_3 and SiO_2 are exposed to radioactive vapors of Mo and Cs at 1100° and 1300°C in air in a sealed chamber. Relative absorption values at 1300°C , extrapolated to short times, yield an approximate relationship $(\text{Mo}) = 1/(\text{Cs})^{1/2}$. The relationship does not apply at 1100°C , below the melting point of most substrates. The relative uptake values of Mo and Cs are strongly related to the composition of the melt, with the oxygen to metal ion ratio playing an important role. Composition sensitivity is somewhat less pronounced at 1100°C , but still significant. The uptake behaviour of both tracers can be correlated to the free oxygen ion activity in the substrates. The Mo and Cs apparently behave like a glass-network forming and a glass-network modifying species, respectively.

INTRODUCTION

In a nuclear explosion molten soil may be exposed to vaporized species of fission products which are present in trace concentrations. The purpose of this work was to devise a relatively simple method for determining the extent to which the composition of the molten oxides might affect volatile or semi-volatile fission product uptake. The results might also have application in generalizing the empirical observations of radiochemical fractionation observed when explosions are conducted over calcareous (coral island) and continental silicate surfaces. The experiments described here were performed at temperatures just below and above the melting points or softening ranges of the condensed matrix oxide systems. The condensed phase itself consisted of oxides found in the earth's crust¹ in a sufficient variety of combinations, such that relationship between substrate composition and relative uptake or absorption of the tracer species in these substrates is revealed.

Norman² has published extensive data on the Henry's law constants of fission product oxide vapor in equilibrium with molten substrates and has developed a fission controlled uptake model for these vapors by the melts. Adams et al³ have focused on the kinetics of the vapor-condensed phase absorption process as a function of temperature, time and nature of the substrate.

As originally envisioned, we had hoped to determine a set of relative Henry's law constants for several vapor oxide species in equilibrium with melts consisting of CaO , Fe_2O_3 , SiO_2 , Al_2O_3 and Na_2O in mixtures of varying compositions. A series of melts were simultaneously exposed to a number of vaporized fission product tracers in a sealed chamber at elevated temperature

for lengths of time considered to be sufficient for attaining equilibrium. Equilibrium was probably not achieved in the experiments as performed, owing to overriding kinetic factors. Our results appear to be better interpreted in terms of "relative attachment coefficients" of the tracer species for certain substrate combinations under given experimental conditions. This paper deals only with the uptake of molybdenum and cesium vapor species, although Sn, Sb, Te, Ru and Rb were included in the experiments. The attachment coefficients of all species appear to be a function of the free oxygen ion activity in the substrates.

EXPERIMENTAL

A. The Method

Given a set of n molten oxides (with the indexes $i, j, \dots$) simultaneously exposed to a vapor containing a radioactive trace element, the equilibrium mol-fractions of the tracer in the different substrates will be related, in this "isopiestic" system, by the expressions

$$K_i N_i = K_j N_j \dots \dots \dots = K_n N_n \quad (1)$$

where the K 's are the Henry's law constants for the given tracer in the several melts.

The experiments were conducted in sealed quartz chambers (Fig. 1) in an ambient pressure of one atmosphere of air at operating temperature. The substrates were in the form of oxide beads, approximately 2.3 mm in diameter suspended from hooks inside the vessel by short platinum loops. The melts (or substrates) in each individual run were of two different composition, one of them being a reference substance which remained constant throughout all the experiments, while the other was varied. Three specimens of each melt type were included in each run. The source, consisting of carrier-free or high specific activity radioactive tracers of Mo-99 and Cs-137, in

addition to other nuclides, was deposited uniformly by evaporation on a quartz plate situated at the bottom of the chamber.

The method of preparing the oxide melts, the preparation of the radioactive sources and details of preparing the sample for radiometric assay are given in the Appendix. The furnace used for heating the samples was a Blue-M Model RG-2090C-1 X, with a peak temperature of 1600°C and a thermoregulator with an accuracy of $\pm 10^{\circ}\text{C}$. The two Pt-Pt (Rh 13%) thermocouples inside the furnace were calibrated with the help of the following standards (m.p. in $^{\circ}\text{C}$ in brackets) : NaCl (801), K_2SO_4 (1069), $\text{Li}_2\text{O} \cdot \text{SiO}_2$ (1202), Diopside $\text{CaO} \cdot \text{MgO} \cdot 2 \text{SiO}_2$ (1392), and nickel (1453). A calibration curve of these standards vs millivolts as measured by a potentiometer was used in order to obtain the desired temperature in each experiment.

The chambers were constructed of fused silica (Thermal American Quartz Co.), and were fabricated by sealing quartz bottoms and tops to rectangular bore tubing. The internal dimensions of the chambers used in most experiments were $50 \times 40 \times 20$ mm, with 2 mm thick walls. A thin quartz rod extended across the top of the chamber (see Fig. 1) served as a holder for the platinum loops containing the molten beads.

The chambers were sealed under reduced pressure, calculated to correspond to one atmosphere at the working temperature, and then heated in the furnace to this predetermined temperature. After the end of reaction, the chambers were removed, cooled, opened and the contents assayed by gamma spectrometry. Each individual substrate was separated from the loop (crushed), weighed and transferred to a plexiglass sample holder that could be held at a fixed geometry with respect to the detector. A similar procedure was followed with the Pt loops and the source wherever possible. The empty

Sealed Quartz Chamber

Figure 1

container was measured separately, at another geometry, and the measures are converted to the geometry of the melts.

The specimens were counted in a fixed 2π geometry on a 30 cubic centimeter lithium-drifted germanium detector with a Tennelec TC-135 preamplifier, Tennelec-200 amplifier, and a Nuclear Data 161 F ADC and 181 M Memory Unit. The resolution of this system (FWHM) is about 2.4 keV for the 662 keV Cs-137 gamma ray. The detection efficiency of the system at maximum geometry is $0.032 (E/E_{140.5})^{-1.2}$ where $E_{140.5}$ is the efficiency of counting the Tc-99 m Mo-99 daughter, and E is the energy of the gamma ray assayed.

B. The Radioactive Source.

The tracers used in most experiments were carrier free or high specific activity solutions. The Mo-99 and Cs-137 tracers were originally introduced as ammonium molybdate and cesium chloride. The amount of Mo-99 tracer per experiment did not exceed 10^{-8} gram-atoms, i.e., 1 μ g of source material, and was often less. Similar quantities of CsCl were used, giving a concentration of 2.5×10^{-10} g-atoms per cm^3 of air inside the chamber. At the above concentrations⁴ the monomer MoO_3 is the most probable species in the gas phase at 1500 K in presence of air; the same is reported also for 1400°C.^{3b} Other calculations based on published free energy data⁶ yield a free energy of formation of -13 kcal/mole for gaseous CsCl at 1573 K as compared to -2.1 kcal/mole for cesium oxide at 1500 K.⁴ This would suggest that conversion to the oxide in the vapor phase is unlikely under our experimental conditions, hence the chloride rather than CsO is assumed to react with the melts.

Both tracers were included in all runs. The nuclides were assayed by measuring the 140.3 keV photopeak of Tc-99 m (equilibrated with Mo-99), and the 662 keV photopeak of Cs-137.

RESULTS

Results are expressed in terms of relative counts per minute of the individual nuclide normalized to unit area of the substrate melt, since it was felt that the important process in these experiments was the attachment rate at the surface of the melt. Tables I and II show the uptake data for Mo-99 and Cs-137 in cpm/cm^2 referred to that in $\text{CaO.FeO}_{1.5}.\text{SiO}_2$ as a standard material; thus, the value for this substrate is always normalized to unity. The value of 0.32 for Mo-99, for example, after 12 hours at 1300°C in $\text{CaO.FeO}_{1.5}.2\text{SiO}_2$ (Table I) means that changing the standard melt by addition of one mole of SiO_2 led to a decrease in the uptake by a factor of about one-third, relative to the standard $\text{CaO.FeO}_{1.5}.\text{SiO}_2$ melt. The values in the tables are averages of one or two triplicate determinations for each combination of substrates. In general, the data for 1300°C are reproducible to about $\pm 10\%$, notwithstanding the considerable uncertainty in the 0.03-0.10 range due to poorer counting statistics. The 1100°C results had larger individual deviation from the average, usually about 20-25%. We noted that some separation of oxide phases sometimes occurred below the melting point of the substrates.

The Mo-99 uptake by the several parts of the system was confined almost entirely to the melts; even the silica plates holding the source retained only a small fraction of the original activity. Typically, 90% of the Mo-99 was found in the melts. The container walls however took up a quite considerable amount of cesium, especially if the melts that were exposed within contained little or no SiO_2 by themselves. Thus, in some experiments as much as 90% of the cesium activity was found on the silica chamber surfaces.

The uptake factor by the clay loam appearing in Tables I and II is not an experimental result but was calculated using data published by Adams et al.^{3b} and appears here only for comparison.

TABLE I

VAPOR UPTAKE FACTORS RELATIVE TO SUBSTRATE I FOR MOLYBDENUM TRACER

(In 2 hour and 12 hour experiments)

Substrates	1300°C 2 hours	1300°C 12 hours	1100°C 2 hours	1100°C 12 hours	m.p. or soft range °C
I $\text{CaO} \cdot \text{FeO}_{1.5} \cdot \text{SiO}_2$	(1.00)	(1.00)	(1.00)	(1.00)	1230-1250 est.
II $\text{CaO} \cdot \text{FeO}_{1.5} \cdot 2\text{SiO}_2$	0.37	0.32	1.0	1.4	1250-1290 est.
III $\text{CaO} \cdot 2\text{FeO}_{1.5} \cdot \text{SiO}_2$	1.26	0.99		0.95	~1250
IV $\text{CaO} \cdot 2\text{FeO}_{1.5}$	11.0	18.0	216.	242.	1250 ^{a)}
V $\text{CaO} \cdot 2\text{FeO}_{1.5}$	1.9	4.4	-	-	1244 ^{b)}
VI $\text{Na}_2\text{O} \cdot 2\text{FeO}_{1.5} \cdot \text{SiO}_2$	0.21	0.13	8.0	2.9	est. 1110-1150
VII $\text{Na}_2\text{O} \cdot \text{SiO}_2$	0.07	0.14	1.2	1.2	1089 ^{a)}
VIII $3\text{CaO} \cdot 2\text{AlO}_{1.5} \cdot 7\text{SiO}_2$	0.07	0.16	4.4	5.6	1165 ^{b)}
IX $3\text{CaO} \cdot 2\text{FeO}_{1.5} \cdot 7\text{SiO}_2$	0.13	0.29	-	-	est. 1260-1280
silica containers	<0.0015	<0.0015			1460-1720 ^{a)}
source on silica plates	<0.04	<0.04			
clay loam	0.7 ^{c)}	0.025 ^{c)}	-	-	

^{a)} from the Handbook of Chem and Phys., 48th ed., 1968^{b)} see ref. 5^{c)} see ref. 3b

TABLE II

VAPOR UPTAKE FACTORS RELATIVE TO SUBSTRATE I FOR CESIUM TRACER

(In 2 hour and 12 hour experiments)

Substrates	1300°C 2 hours	1300°C 12 hours	1100°C 2 hours	1100°C 12 hours	O/Si ratio
I $\text{CaO} \cdot \text{FeO}_{1.5} \cdot 2\text{Si}$	(1.00)	(1.00)	(1.00)	(1.00)	4.50
II $\text{CaO} \cdot \text{FeO}_{1.5} \cdot 2\text{SiO}_2$	16.0	12.0	1.8	0.89	3.25
III $\text{CaO} \cdot 2\text{FeO}_{1.5} \cdot \text{SiO}_2$	0.41	0.45	0.22	0.70	6.00
IV $\text{CaO} \cdot 2\text{FeO}_{1.5}$	0.04	0.1	0.7	2.8	--
V $\text{CaO} \cdot 3\text{FeO}_{1.5}$	0.03	0.02	--	--	--
VI $\text{Na}_2\text{O} \cdot 2\text{FeO}_{1.5} \cdot \text{SiO}_2$	31.	47.	98.	113.	6.00
VII $\text{Na}_2\text{O} \cdot \text{SiO}_2$	27.	66.	36.	89.	3.00
VIII $3\text{CaO} \cdot 2\text{AlO}_{1.5} \cdot 7\text{SiO}_2$	122.	49.	28.	43.	2.86
IX $3\text{CaO} \cdot 2\text{FeO}_{1.5} \cdot 7\text{SiO}_2$	37.	9.3			2.86
silica containers					
for melts II, III	~0.24	~0.39	0.38-0.47	0.24-0.38	2.00
for melt IV	0.94	1.3	0.69	1.9	
for melts VI-IX	0.01-0.2	0.01-0.15			

ASPECTS OF EXPERIMENTAL DESIGN

A. Significance of the Sealed Chamber Measurements.

In our experimental design there are three distinct substances that could react with the tracer vapor:

- (1) the quartz chamber walls (78 cm^2),
- (2) the oxide bead of spherical form, usually in two compositions, each in triplicate ($1-2 \text{ cm}^2$),
- (3) the platinum loops ($.01 \text{ cm}^2/\text{gm}$).

The criterion for true equilibrium mentioned in the experimental part would imply that the system as a whole and all its components reach a steady state or, at least, a condition of slowly changing distribution of the tracer between all components. In addition, a uniform concentration of the tracer throughout each melt is required, as well as a rate of escape from the liquid surface just balanced by the rate of return from the vapor phase. Other factors favoring equilibrium are high volatility of the tracers and their rapid uptake by the melts, and favorable diffusion coefficients of the tracers in the melts.

Calculations of equilibrium vapor pressures of Cs and Mo oxide vapors over the $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ eutectic (of a composition similar to melt VIII) at 1300°C were performed with the help of Norman's equation for the Henry's law constants.^{2d} These indicate that the fraction of Mo remaining in the gas phase at equilibrium is about 3.0×10^{-6} , and for Cs about 3.5×10^{-5} .

Adams et al.³ found the uptake of MoO_3 and TeO_2 vapor species by calcium ferrite to be proportional to the diameter of the substrate and showed that the rate determining step in this case is diffusion of the tracer molecule in the vapor phase to the liquid droplet surface, over a wide range of temperatures and partial pressures.

B. First Order Kinetics Approximation.

The amounts of high specific activity Mo and Cs tracers used simultaneously in each run were between 10^{-9} to 10^{-11} gram-atoms as compared with the millimole amounts of the substrates; it is therefore reasonable to assume first order kinetics for release and uptake of the tracers in the course of the experiment.

Each source consists of N_s^0 atoms, originally present at the bottom of the chamber. On heating, atoms are assumed to be expelled at a rate proportional to their number in the source:

$$- dN_s/dt = k_s N_s \quad (2)$$

k_s being the first order release rate constant of the source in fraction per unit time. Each component of the system is assumed to absorb the radioactive species at a rate proportional to the fraction of molecules in the gas volume impacting on a unit area of substrate per unit time ϕ , the attachment coefficient a and the area of substrate s . It is also assumed that the release from the substrate occurs at a rate proportional to the number of atoms already absorbed, and therefore a partial release rate constant or release coefficient b can also be assigned to each component. The units of b are $\text{cm}^2 \cdot \text{min}^{-1}$. This is obviously only an approximation since the release rate is diffusion controlled and depends upon the distribution of the tracer within the volume of the substrate. We can define for the whole system an overall uptake factor k_1 and an overall release rate constant k_2 ; each includes the respective values of a and b for melt i , the reference melt j , the silica container walls and the platinum loops:

$$k_1 = \phi (a_i \cdot s_i + a_j \cdot s_j + a_{\text{SiO}_2} \cdot s_{\text{SiO}_2} + a_{\text{Pt}} \cdot s_{\text{Pt}}) \quad (3a)$$

$$k_2 = b_i \cdot s_i + b_j \cdot s_j + b_{\text{SiO}_2} \cdot s_{\text{SiO}_2} + b_{\text{Pt}} \cdot s_{\text{Pt}} \quad (3b)$$

In all subsequent treatments, the subscript _j will designate the reference melt $\text{CaO.FeO}_{1.5}.\text{SiO}_2$.

If we designate the total number of gaseous atoms in the chamber volume as N_g and the number of atoms taken up by the melts or deposited in any part of the system as N_m ,

$$dN_g/dt = k_s N_s - k_1 N_g + k_2 N_m \quad (4)$$

Making use of the fact that $N_s^0 = N_s^0 \exp(-k_s t) + N_m + N_g$, and using the boundary condition $N_g = 0$ at $t = 0$,

$$N_g = N_s^0 \left\{ \frac{k_s - k_2}{k_1 + k_2 - k_s} \exp(-k_s t) - \frac{k_1 k_s \exp \left[- (k_1 + k_2) t \right]}{(k_1 + k_2 - k_s) (k_1 + k_2)} + \frac{k_2}{k_1 + k_2} \right\} \quad (5)$$

The uptake as a function of time by a given melt (for example i) is given by

$$dN_i/dt = a_i \phi_i s_i N_g - b_i s_i N_i \quad (6)$$

where the first term on the right indicates the number of absorbed gaseous molecules, and the second term the released ones, per unit time. By substituting the expression for N_g in Eq. (5) and solving for N_i , we obtain

$$N_i = a_i s_i \phi_i N_s^0 \left\{ \frac{(k_s - k_2) \exp(-k_s t)}{(k_1 + k_2 - k_s) (b_i s_i - k_s)} - \frac{k_1 k_s \exp \left[- (k_1 + k_2) t \right]}{(k_1 + k_2 - k_s) (k_1 + k_2) [b_i s_i - (k_1 + k_2)]} + \frac{k_s (b_i s_i - k_2) \exp(-b_i s_i t)}{b_i s_i (b_i s_i - k_s) [b_i s_i - (k_1 + k_2)]} + \frac{k_2}{(k_1 + k_2) b_i s_i} \right\} \quad (7)$$

Equations similar to Eq. (6) and (7) can also be written for the reference melt j . In case of very long heating times, when $t \approx \infty$, the ratio of the activities of the two substrates becomes, with respect to the same tracer,

$$N_i/N_j = \frac{a_i/a_j}{b_i/b_j} \quad (8)$$

since $\phi_i = \phi_j$.

If $k_s \gg k_2 > b_1 s_1$, and $k_1 \sim k_s$, corresponding to release from the source, comparable to the melt acquirement rate, and rapid pickup by the melts relative to reemission by the melts,

$$N_i = a_i s_i \phi_i N_s^0 \left[\frac{e^{-k_s t}}{k_s - k_1} - \frac{e^{-k_1 t} k_s}{k_1 (k_s - k_1)} + \frac{b_1 s_1 - k_2}{k_1 b_1 s_1} e^{-b_1 s_1 t} + \frac{k_2}{(k_2 + k_1) b_1 s_1} \right] \quad (9)$$

This case is obtained by dropping small terms in equation (7).

Of more interest is when the rate of release by the source and the rate of uptake by the melts takes place in a time short compared to the rate of release in the reverse direction by the melts and the duration on the experiment. (This corresponds to the situation of favorable Henry's law constants for absorption by the melts, a condition which obtains for most of the species studied.)

For this case:

$$k_s t \gg 1, k_1 t \gg 1, k_1 \sim k_s \text{ and } e^{-k_s t} \rightarrow 0, e^{-k_1 t} \rightarrow 0 \text{ and } N_i/N_j$$

becomes:

$$\frac{N_i}{N_j} = \frac{a_i/b_i}{a_j/b_j} \left[\frac{(\frac{b_1 s_1}{k_2} - 1) e^{-b_1 s_1 t} + 1}{(\frac{b_j s_j}{k_2} - 1) e^{-b_j s_j t} + 1} \right] \quad (10)$$

It can be seen from (10) that when $t \rightarrow 0$, $N_1/N_j \rightarrow a_1/a_j$, or the ratio of attachment coefficients.

This means that the relative attachment coefficients can be determined directly from relative counting rates provided the heating times are kept short enough. An illustrative calculation using Eq. (9) is given in Table III for the following three cases which fall within the range of typical values found:

$$\begin{aligned} b_1 \cdot s_1 &= 0.001 & \text{and } b_1/b_j &= 0.1 \\ b_1 \cdot s_1 &= 0.005 & \text{and } b_1/b_j &= 0.5 \\ \text{and } b_1 \cdot s_1 &= 0.2 & \text{and } b_1/b_j &= 2. \end{aligned}$$

It is obvious that with heating times of 15 minutes or less, only minor corrections would be required to obtain the attachment coefficient ratio by use of Eq. (10). It is also seen from Table III and Eq. (9) that the higher the b_1/b_j ratio, the shorter is the time required to attain equilibrium, which is one of the conditions for evaluating the Henry's law constants.

EVALUATION OF ATTACHMENT AND RELEASE COEFFICIENTS

Samples that had previously been loaded with radioactivity at 1100°C during the sealed chamber experiments, were reheated at 1300°C for times ranging from 25 to 60 minutes. After assay the sample was returned to the furnace and the heating was repeated. These measurements are presented in Table IV as fractional loss rates per cm^2 of the releasing surface of the melt per minute at 1300°C . The measurements provide an indication of the manner in which the release rate depends upon the substrate type and how it affects the two and twelve hours measurements appearing in Tables I and II.

TABLE III

EFFECT OF ASSUMED RELEASE RATE FROM THE MELTS ON THE

Time (min)	ESTIMATION OF a_1/a_j		
	$\frac{N_1/N_j}{a_1/a_j}$ for $b_1/b_j = 2$	$\frac{N_1/N_j}{a_1/a_j}$ for $b_1/b_j = 0.5$	$\frac{N_1/N_j}{a_1/a_j}$ for $b_1/b_j = 0.1$
0	1.00	1.00	1.00
15	0.88	1.07	1.14
30	0.81	1.13	1.27
60	0.71	1.24	1.53
120	0.61	1.41	1.98
360	0.51	1.80	3.67
600	0.5	1.93	5.03
720	0.5	1.96	5.59
Infinite	0.5	2.00	10.00
b_1/a_j (min ⁻¹)	0.2	0.005	0.001

In addition, the release rate of the tracers from a quartz surface was investigated. Tracers were evaporated onto a known area of quartz plate and then expelled by heating at 1300°C. The plates were counted after each heating in fixed geometry on a low-background beta counter. In all cases there was an initial rapid decrease of activity with time followed by a much flatter portion of the expulsion curve. These data were analyzed into two (nearly exponential) components: The rapid first step might be considered to be proportional to the release rate constant k_s of the source (see Eq. (2)), while the second one might be construed as the release coefficient for silica, b_{SiO_2} in Eq. (3b). Table IV also includes the relative attachment coefficients of Mo and Cs tracers in substrates II through VIII (referred to Melt I as standard). These were calculated from Eq. (9). The estimated b values used in the calculation were those in Table IV. The relative uptake factors (attachment coefficients) of Mo and Cs follow the approximate empirical relationship $(a_i/a_j)_{\text{Mo}} \approx [(a_i/a_j)_{\text{Cs}}]^{1/2}$ as shown in Fig. 2 (see also Table IV).

DISCUSSION

A. Some Structural Aspects of Silicate Melts

X-ray analysis showed most of our silicate melts to be glassy, amorphous substances. According to Zachariasen and others ^{7,8}, such glasses consist of a random discontinuous network of silicate tetrahedra, linked together by sharing an oxygen. The glasses do not contain discrete oxide molecules, but are rather made up of the following species: large oxygen ion (free or bound to silica), small lattice-forming ions of high positive charge (Si^{4+} , P^{5+} , B^{3+} , Al^{3+} , Fe^{3+}) and modifying cations with large

TABLE IV

AVERAGE RELEASE RATES AND RELATIVE ATTACHMENT COEFFICIENTS

AT 1300° C

SUBSTRATES	Mo	Cs	Mo	Cs	Cs
	$b \text{ cm}^{-2} \text{ min}^{-1}$	$b \text{ cm}^{-2} \text{ min}^{-1}$	a_1/a_j	a_2/a_j	$(a_1/a_j)^{-1/2}$
I (j)	0.021	0.042	1.0	1.0	1.0
II	0.015	0.054	0.26 ± 0.06	16.1 ± 1.0	0.25
III	0.051	0.008	2.3 ± 0.1	0.10 ± 0.02	3.2
IV	0.005	0.089	5.2 ± 0.7	0.14 ± 0.04	2.6
V	-	-	-	-	-
VI	0.078	0.088	0.05 ± 0.01	66 ± 13	0.12
VII	0.042	0.021	0.25 ± 0.09	19 ± 5	0.23
VIII	0.008	0.002	0.09 ± 0.03	41 ± 18	0.16
silica	0.0024	0.0007			

	Mo	Cs
$k_g(\text{SiO}_2)$	0.089 min^{-1}	0.328 min^{-1}

Figure 2

radia (Ca^{2+} , Na^{2+}) which neutralize the excess negative charge and fill out the lattice holes (ref. 7,9,10,11). According to N'aray-Szabo¹⁰ the oxygen to cation distance in lattice-forming oxides does not exceed 1.80 Å and therefore only ions of tetrahedral coordination may be included amongst glass-forming elements (in addition to boron). Weyl⁸ has stressed the importance of the bridging and non-bridging oxygens in the silicate-glass structure, and their interaction with cations of the alkalis and alkaline earths. Such interactions within metallurgical slags were treated theoretically by Toop and Samis¹², and Yokokawa and Hiwa¹³, who showed a way to evaluate oxygen ion activities from thermodynamic data. Douglas et al¹⁶ found that the redox-equilibria in alkali silicate glasses shift towards the oxidized state with increasing basicity of the glass and a corresponding decrease in oxygen ion activity. This is explained by Budd¹⁷ as being due to the reaction

as compared to the quite different effect in the less alkaline soda-lime silicate glasses:

The predominance of the trivalent iron complex (Eq. 11) in silicates of a high Na_2O content (>30%) above 1200°C was also confirmed by others.¹⁸ Weyl⁸ emphasized the role that minute additions of foreign ions may play in affecting the surface tension and the fact that the surface zone may have different properties from the bulk liquid. A possible greater reactivity of the surface is of immediate concern in this investigation where a foreign vapor enters at the surface of a liquid droplet. Diffusion from the surface into the bulk liquid and counter-diffusion occur probably

simultaneously, thus replenishing the surface previously modified by absorption of the foreign vapor species.

Increasing the O/Si ratio is known to decrease the viscosity of the melts and reduce their liquidus temperatures. This is explained as being due to depolymerization of the three-dimensional framework when oxygen ions are introduced in the form of an oxide containing a cation of a weak field strength.^{11,12} Some field strength values of cations discussed in this work are listed in Table V. The lower the field-strength, the greater the degree of depolymerization, which evidently is a function of the competition between Si^{4+} and the cations for oxygen.

B. Relationship Between Uptake and Melt Composition

Comparison of the uptake in calcium iron silicates of various compositions in Tables I and II reveals a qualitative relationship between the N_i/N_j values (j = Melt I, i = other melts) and the O/Si ratios. The addition of silica in melts II and IX, as compared to the standard substance I suppresses the Mo and enhances the Cs uptake, while an excess of iron oxide produces the opposite effect as seen in Melt III. The two melts with a higher O/Si ratio (I and III) are structurally composed of silicate groups with, perhaps, an excess of non-bridging oxygen as compared to the other two melts II and IX which probably still contain partly polymerized chains. According to Kochkin²⁰ a "neutral" silicate of this type should have a O/Si ratio of 3.38, a value which he obtained graphically by plotting $\log \text{Fe}^{3+}/\text{Fe}^{2+}$ versus O/Si for various "acidic" and "basic" minerals.

It will be seen later that the higher the "basicity" of a melt, the greater is its oxygen ion activity under identical experimental conditions. This would explain the increased uptake of the acidic MoO_3 tracer by the

"basic" melts I, II and IV in accordance with the reaction

and the decreasing uptake by "acidic" melts II, IX, VII and VIII (see Table I). The low uptake of Mo tracer in Melt VI as compared to III is of course due to the low (O^{2-}) activity of the former which in turn is a consequence of the different field strength of Na^+ and Ca^{2+} (see Table V).

The uptake pattern of cesium was exactly the opposite of that of Mo. The tracer vapor, in the form of $\text{Cs}^+ \text{X}^-$ (X being Cl or O), apparently reacts as a network modifier: the greater the degree of polymerization of the still remaining tetrahedral silicate chains, the higher the uptake of cesium, so that we may anticipate a pick-up behavior inversely proportional to the (O^{2-}) activity at the surface. This would also explain the relatively high uptake by the silica container (see Table II). Aluminum is known for its ability to replace silicon as a glass-forming element by coordination of four oxygens. Ferric iron is said to have similar properties²¹, although these are probably less pronounced. The data in Tables I and II are consistent with the view that the Al-containing Melt VIII is more "acidic", which means that its (O^{2-}) activity is lower than in Melt IX (see also field-strength data in Table V). The sodium-containing melts VI and VII will be discussed later.

C. Field Strength Parameter Correlations

Dietzel¹¹ has achieved considerable systematization of the properties of glasses by using the concept of the field strength parameter $z/(r_c + r_a)^2$, where the denominator is the sum of the cation and the oxygen anion radii and z the charge on the cation (see Table V). This parameter is a measure of the force binding the O^{2-} ion to the cations in its environment.

TABLE V

IONIC RADII AND FIELD STRENGTHS OF CATIONS

(Dietzel, ref. 11)

Cations.	Coordination	Ionic Radii $r_c (\text{\AA})$	$1/r_c^2$ *
Ca^{+}	8	1.65	0.10
K^{+}	8	1.33	0.13
Na^{+}	8	0.98	0.19
Li^{+}	6	0.78	0.23
Ca^{2+}	6 (8)	1.06	0.33
Fe^{2+}	6	0.83	0.43
Mg^{2+}	6	0.78	0.45
Al^{3+}	4 (6)	0.57	0.97
Fe^{3+}	4 (6)	0.67	0.85
Mo^{6+}	4	0.62	1.79
Si^{4+}	4	0.39	1.57

$$* a = r_c + r_a; r_a(\text{O}^{2-}) = 1.32 \text{ \AA}$$

We define an average field strength factor per atom of oxygen for a melt containing n_1 atoms of cation of field strength f_1 and m atoms of oxygen as:

$$\bar{f} = \frac{\sum n_i f_i}{m} \quad (14)$$

The quantity $\Delta \bar{f}$ is defined as $\bar{f} - \bar{f}_g$, $\bar{f}_g$ being the value for the standard reference melt I. Calculated values for $\Delta \bar{f}$ for the various melts are presented in Table VI. The relative uptake data N_1/N_j for the two-hour experiments are plotted against $\Delta \bar{f}$ in Fig. 3. The two straight lines were obtained through a least square calculation of the Mo and Cs data respectively. They correspond to an expression

$$\ln(N_1/N_j) = a (\Delta \bar{f}) + b$$

with the constants a and b having the following values:

$$\text{for Mo, } a = -19.3 \pm 3.5 \text{ and } b = 0.62 \pm 0.29$$

$$\text{for Cs, } a = 48.5 \pm 4.0 \text{ and } b = 0.15 \pm 0.20.$$

Correlation between $\Delta \bar{f}$ and N_1/N_j is fairly good considering the experimental uncertainties and the arbitrariness in the definition of $\Delta \bar{f}$. The only exception from the general pattern is the sodium iron silicate substrate (Melt VI) whose uptake values for Mo and Cs are identical to those of sodium meta-silicate (Melt VII) within experimental error. The addition of one mole of Fe_2O_3 does not seem to have any effect on the uptake. The weak interaction between Na^+ and O^{2-} (in Na_2O) leads to a preemption of the oxide ions by iron in accordance with Eq. (11) resulting in a very low free oxygen ion activity, which is probably not much different from that of sodium meta-silicate. The $\Delta \bar{f}$ values are apparently only a crude measure of this activity in binary or ternary oxide mixtures which have similar cationic components. Electrochemical measurements of the oxygen

TABLE VI

THE FIELD STRENGTH PARAMETER $\bar{f} = \frac{\sum \bar{f}_i r_i}{n}$ OF THE SUBSTRATES

Substrates	Atomic ratios	$\bar{f}$	$\Delta \bar{f}$	Results of x-ray analysis
(1)	$\text{CaFeSiO}_{4.5}$	.596	0	amorphous matter
(2)	$\text{CaFeSi}_2\text{O}_{6.5}$	.653	+.057	" "
(3)	$\text{CaFe}_2\text{SiO}_6$	.574	-.022	" "
(4)	CaFe_2O_4	.467	-.129	single compound
(5)	$\text{CaFe}_3\text{O}_{5.5}$	.478	-.118	mixture of $\alpha\text{-Fe}_2\text{O}_3$ and CaFe_4O_7
(6)*	a) $\left. \begin{array}{l} \text{Na}_2\text{Fe}_2\text{O}_4 \\ \text{SiO}_2 \end{array} \right\}$	.475 (-.121) .785 (+.189)	.068	$\alpha\text{-Fe}_2\text{O}_3$ identified but no Na_2SiO_3 , which is probably amorphous.
(7)	Na_2SiO_3	.650	+.054	mixture of 2 probably 3 SiO_2 compounds.
(8)	$\text{Ca}_3\text{Al}_2\text{Si}_7\text{O}_{20}$	.687	+.091	amorphous matter
(9)	$\text{Ca}_3\text{Fe}_2\text{Si}_7\text{O}_{20}$	.687	+.082	not analyzed
(10)	clay loam ^{b)}	.586	-.01	

a). $(\text{FeO}_2)^{-}$ above 1200°C is the prevalent Fe-species if the mole fraction is larger than or equal to 0.3. Ref. (18).

b). Estimated from the data of C.E.Adams et al., USNRDL-TR-67-98 (1967).

* Calculation in this manner leads to correlation of $\text{Na}_2\text{O} \cdot 2\text{Fe}_2\text{O}_3 \cdot 1.5\text{SiO}_2$. If calculated directly $\bar{f} = .579$ and $\Delta \bar{f} = -0.014$.

Figure 3

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5 CYCLES X 12 DIVISIONS PER INCH

$\frac{Z_i}{Z_j}$

UPTAKE FACTORS vs Δf
AT 1300°-12 HRS.

↕ Cs.

I Mo.

potential of the cell $\text{PbO.SiO}_2\text{-PbO.SiO}_2 + n\text{R}_x\text{O}_y/\text{O}_2^{22}$, functioning as an oxygen concentration cell, showed the emf's for the alkali metal ions Na^+ and K^+ to be very low relative to the alkaline earth ions; only the latter manifested a fairly smooth behaviour as a function of field strength, in the same family as Si^{4+} and Al^{3+} .

D. Estimation of Oxygen Ion Activity

It might be postulated from the foregoing that the attachment coefficients of Mo and Cs vapor species are related to the free oxygen ion activities in the molten substrates. This activity should be the highest in calcium ferrite^(IV) and should progressively decrease for the melts $\text{CaO.2FeO}_{1.5}\text{.SiO}_2^{(\text{III})}$, $\text{CaO.FeO}_{1.5}\text{.SiO}_2^{(\text{I})}$, $\text{CaO.FeO}_{1.5}\text{.2SiO}_2^{(\text{II})}$, $3\text{CaO.2FeO}_{1.5}\text{.7SiO}_2^{(\text{IX})}$, $3\text{CaO.2AlO}_{1.5}\text{.7SiO}_2^{(\text{VIII})}$, $\text{Na}_2\text{O.SiO}_2^{(\text{VII})}$, and $\text{Na}_2\text{O.2FeO}_{1.5}\text{.SiO}_2^{(\text{VI})}$ in respective order.

Toop and Samis¹² proposed a thermodynamic model for simple silicate melts by interrelating the number of bridging (O^0), non-bridging (O^-) and free oxygen ions per mole of silicate according to

Eq. (15) is a simplified form of the reaction

which is common to all silicates whether they are well defined compounds or mixtures of oxides. The equilibrium constant k

$$k = \frac{(\text{O}^0)(\text{O}^{2-})}{(\text{O}^-)^2} \quad (17)$$

is temperature dependent and characteristic of the kind of cations present in the binary or ternary silicate melt, but is independent of their molar ratios. This means that all the melts consisting, for example, of FeO and

SiO_2 in various proportions should have the same k at a given temperature.

Other useful equations are

$$(O^0) = \frac{4N_{\text{SiO}_2} - (O^-)}{2} \quad (18)$$

$$4k = \frac{\left[4N_{\text{SiO}_2} - (O^-)\right] \left[2 - 2N_{\text{SiO}_2} - (O^-)\right]}{(O^-)^2} \quad (19)$$

where N_{SiO_2} indicates the mole fraction of silica. k is related to the molar free energy of mixing of the oxide and silica, using the approximation

$$\Delta G(\text{mix}) = RT \left[\frac{(O^-)}{2} \right] \ln k \quad (20)$$

In addition, Toop and Samis assumed certain k -values for the systems

CaO-SiO_2 and FeO-SiO_2 at 1600°C and applied the ionic form of the Gibbs-Duhem equation to calculate activities of the ferrous, calcium and oxygen ions.¹² A somewhat different approach based on a quasi-lattice treatment

of the random network model was used by Yokokawa and Niwa¹³ who developed the following expression for the free energy of solution (mixing) of binary and ternary silicates:

$$\begin{aligned} \frac{\Delta G}{R T} = & \frac{3}{2} X \ln X - 3(1-X) \ln 2(1-X) + \frac{2-X}{2} \ln(2-X) + X \ln \left[X - \frac{(O^-)}{2} \right] + \\ & 2(1-X) \ln \left[2(1-X) - \frac{(O^-)}{2} \right] + X_1 \ln \frac{X_1}{X} + X_2 \ln \frac{X_2}{X} \end{aligned} \quad (21)$$

In Eq. (21) X_1 and X_2 are the mole fractions of the two basic oxides respectively and $X = X_1 + X_2$. In addition to the mixing effect as expressed by Eqs. (15) and (16), a chemical reaction of the type

can take place, for which the following well known expression holds

$$\Delta G^\circ + -RT \ln K \quad (23)$$

ΔG° indicating the standard molar free energy change of the reaction in

Eq. (22), and K being its equilibrium constant. Yokokawa and Niwa^{13b} used the logarithmic mean to calculate equilibrium constants for ternary melts

$$\ln \bar{K} = \frac{X_1}{X_1 + X_2} \ln K_1 + \frac{X_2}{X_1 + X_2} \ln K_2 \quad (24)$$

and proposed the following expression for the free oxygen ion activity therein:

$$a(O^{2-}) = \frac{2X - (O^{2-})}{(2 - X)} \frac{2k}{K} \quad (25)$$

Equations 15-25 were used to calculate the oxygen ion activities for a number of binary silicate melts in the range of 1550°C to 1600°C and listed in Table VII together with the data of Toop and Samis. The calculations are based on some known values of ΔG° and $\Delta G(\text{mix})$ ^(12,14-16,23-27) and indicate that it is possible to obtain fairly comparable results by the two independent ways mentioned above.^{12,13} The free oxygen ion activity data for the binary silicates in Table VII and for ternary melts in Table VIII are only qualitatively comparable with our relative attachment coefficients due, among other things, to the fact that our experiments were performed at 1300°C, while the calculations are for 1550°C to 1600°C. Some free energy data at 1300°C have been reported for sodium silicate^(15,23), fayalite ($2\text{FeO} \cdot \text{SiO}_2$) and ferrosilite ($\text{FeO} \cdot \text{SiO}_2$)²⁸ but are useless for the present consideration as no data are known on calcium silicate or the $\text{Fe}_2\text{O}_3 - \text{SiO}_2$ system at this temperature. In fact, the only data on "ferric silicate" (see Table VII) were taken from a graph by Turkdogan²⁵ showing a plot of the free energy of solution (mixing) versus composition at 1550°C, when the $(\text{Fe}^{2+} + \text{Fe}^{3+})/\text{Fe}^{2+}$ ratio is about 3.5²⁹. Ferric oxide and silica are reported not to form compounds³⁰ but only mixtures, due to the almost neutral character of Fe_2O_3 ¹³ and therefore equations 22, 23, 24, 25 are not

TABLE VII

ESTIMATED OXYGEN ION ACTIVITIES FOR SOME BINARY SILICATES (1550°-1600° C)

Melts	ΔG° Kcal/mole	K	ref	ΔG°_{mix} Kcal/mole	k	ref	(O^{2-}) fraction	(O^{2-}) estimated	$a(O^{2-})$ lit	ref
$K_2O \cdot 2SiO_2$	-76.8		(19)	-27	3×10^{-10}	(15)	2/3 1	10^{-10} *	2.1×10^{-8}	(15)
$Na_2O \cdot 2SiO_2$	-64.4		(23)	-18	5.1×10^{-7}	"	2/3 1	2.2×10^{-7}	1.9×10^{-6}	"
$Na_2O \cdot SiO_2$	-50.7	1.2×10^{-6}		-24	2.6×10^{-6}	"	1 0.5	5.1×10^{-6}	3.2×10^{-4}	"
$Li_2O \cdot SiO_2$				-16.5	1.4×10^{-4}	"	~1 ~0.5	2.9×10^{-4}	~0.0017	"
$2Na_2O \cdot SiO_2$					"		4/3 0			
$CaO \cdot SiO_2$	-21.7	0.003	(24)	-12.2	0.0017	(12)	0.99 0.5	0.005 *	0.003	(12)
$2CaO \cdot SiO_2$	-34	1.1×10^{-4}	(26)	-15	"	"	1.33 0.002	0.066	0.05	"
$CaO \cdot 2SiO_2$	-7	0.15	(23)	-8.5	"	"	0.66 ~1	0.003	0.003	"
$2FeO \cdot SiO_2$	-5.8	0.2	(25)	-2.2	0.17	(12, 13 27)	0.68 0.33	0.65 *	0.57	(12)
$FeO \cdot SiO_2$	-3.5	0.39	(23)	-2.2	"	"	0.66 0.67	0.2	0.35	"
$4FeO \cdot SiO_2$		0.37	***	-1.75	"	"	0.53	-	0.83	"
$2FeO_{1.5} \cdot SiO_2$				-2.8	0.32	(25)	0.72 0.31	0.49 ***		
$FeO_{1.5} \cdot SiO_2$					"		0.58 0.71	0.15		
$4FeO_{1.5} \cdot SiO_2$					"		0.55 0.12	0.8		
$6Al_2O_3 \cdot 2SiO_2$	-5.7	0.22	(24)	-0.72	0.19	(24)	0.72			
$2Al_2O_3 \cdot SiO_2$	-0.3	0.92	(23)		"		0.84 0.25 st	0.54 *		

TABLE VII (Cont'd)

Footnotes:

- * —→ estimated using Eqs. (17), (18)
- ** —→ estimated using Eq. (16); see also data in ref. 15
- *** —→ estimated from Eqs. (17), (18), (22), (24); see also ref. 13
- **** —→ estimated using Eqs. (16), (17), (18) with ΔG_{mix} value from ref. 25
- ***** —→ estimated using Eqs. (16), (17), (18), (20)
- ***** —→ estimated using Eq. (24) and $a(\text{O}^{2-})$ from ref. 12
- ** —→ equal to Charles' values for $a(\text{H}_2\text{O})$

applicable. Details of the calculations can be found in the appendix.

It is evident from Table VII that the oxygen ion activity increases when the molar free energy of formation of the silicate (from its oxide components) becomes less negative. A similar trend occurs also for the molar free energy of mixing which is proportional to $\ln k$, a high value of k giving more available (O^{2-}) ions than a low value (see Eq. 17). It is also evident from comparison with Table V that the (O^{2-}) activity increases with increasing cationic field strength, resulting in increased polarization of the oxygen and a more stronger shift to the right in Eq. 15. For melts having identical cations the free oxygen ion activity increases in the following order: $R_a O_b \cdot 2SiO_2 < R_a O_b \cdot SiO_2 < 2R_a O_b \cdot SiO_2$, etc. The single bonded oxygen concentration, however, is highest for melts of the type $2R_a O_b \cdot SiO_2$.^{13b} The data on "ferric-silicate" are probably the least accurate as they are all based on an extrapolation; however, the calculated results should be lower than those for their divalent counterpart, which they in fact are. It is interesting to note that Pauling³¹ assigned to ferric iron an electronegativity 1.9 as compared to 1.8 for ferrous iron.

The estimated free oxygen ion activities for the ternary melts in Table VIII compare well in a qualitative sense with the relative attachment coefficients in Table IV for the calcium containing melts. $CaO \cdot 2FeO_{1.5}$ contains less ferric oxide than $CaO \cdot 3FeO_{1.5}$ and we might expect a corresponding higher (O^{2-}) activity, which is actually demonstrated by the higher uptake of Molybdenum. Our assumed value of $a(O^{2-}) = 1$ for $CaO \cdot FeO_{1.5}$ compares well with its large a_1/a_2 ratio as well as with the findings of Adams et al.^{3b} that the uptake of Mo in this substance corresponds to the theoretically, calculated impact rate. Calculation on the CaO-FeO system

TABLE VIII

OXYGEN-ION ACTIVITIES FOR TERNARY MELTS IN THE RANGE 1550°-1600° C

Comparison of reported values with those estimated from
thermodynamic data.

Melts from the Literature	Estimated ln K	ln k	Fractions (o ⁻) (o ⁰)	a(O ²⁻) Est.	a(O ²⁻) Lit.	Ref.
CaO.2FeO				**	1	(12)
CaO.2FeO.SiO ₂	-3.45	-4.08	0.93	0.48	0.5	"
CaO.FeO.SiO ₂	-4.24	-5.23	0.85	0.27	0.2	
CaO.FeO.2SiO ₂	-3.38	-4.08	0.83	0.12	0.08	
3CaO 2FeO.7SiO ₂	-4.07	-5.23	0.66	0.067	0.04	
Melts Investigated			* **	**		
I CaO.FeO _{1.5} .SiO ₂	-3.76	1.02	0.16	0.16		
II CaO.FeO _{1.5} .2SiO ₂	-3.76	0.78	0.61	0.03		
III CaO.2FeO _{1.5} .SiO ₂	-3.76	0.87	0.07	0.26		
IV CaO.2FeO _{1.5}				assumed =1		
IX 3CaO.2FeO _{1.5} .7SiO ₂	-5.07	0.69	0.82	0.004		
VIII 3CaO.2AlO _{1.5} .7SiO ₂	-5.20	0.71	0.81	0.003		
VII Na ₂ O.SiO ₂	-13.6	-12.88	1	0.5	5.1x10 ⁻⁶	(15)
VI Na ₂ O.2FeO _{1.5} .SiO ₂		0.87	0.07	0.01		

* —→ averages of values from Table VII

** —→ estimated using Eq. (24)

** —→ estimated using Eqs. (16)(17)

by Toop and Samis¹² indicate a unit activity over the whole range of composition, probably due to more basic character of ferrous oxide.

CONCLUSION

The sealed chamber technique has proven useful in revealing a significant relationship between the uptake of trace fission product vapors and composition of binary and ternary oxide melts. However, these two hour and 12 hour exploratory runs were too long to represent attachment coefficients and too short for the evaluation of Henry's Law constants. Some improvements in the experimental technique such as source preparation and shorter heating times would greatly improve the usefulness of the method, especially in view of the very sensitive correlation between the uptake values and the free oxygen ion activity of the substrates. Future experiments should be directed towards the possibility to measure this activity directly by electrochemical methods and to obtain correlations with uptake coefficients using Mo and Cs tracers.

A P P E N D I X A

Preparation of Oxide Melts

The following analytically pure substances were used to prepare the melts: anhydrous Na_2SiO_3 , Al_2O_3 , Fe_2O_3 , Fe_3O_4 , SiO_2 , CaCO_3 and $\text{Na}_2\text{CO}_3 \cdot 1/2 \text{H}_2\text{O}$. All were dried at standard analytical conditions, except SiO_2 which was obtained from silicic acid by expelling the crystallized water through prolonged heating at 1300°C . The above substances were thoroughly mixed in a powdered form, according to a stoichiometric ratio that would yield between 0.5 to 1 gram of each desired melt. The oxide mixtures were melted in (open) Pt crucibles in air, for several hours or overnight, and at a temperature which exceeded their m.p. by 50 to 100 degrees. Sodium-containing mixtures were melted only for 1/2 hour to minimize the loss of Na_2O through evaporation.

Preparation of the Substrate Sample

Platinum wire of 0.008" thickness (B. and S. gauge 32) was used for sample preparation by cutting it into pieces 25 mm long and making a small loop at one end. These loops were repeatedly immersed into the liquid melts inside the hot furnace followed by cooling at room temperature. The substrates within the loops were remelted in an acetylene torch until they assumed a spherical form with a measurable diameter of 2 to 3 mm. The weight of these melts varied between 10 to 40 mg; that of the platinum loop was about 20 mg. All the substrates were annealed for about 2 hours 100 to 150

degrees above their respective melting points ($\text{Na}_2\text{O} \cdot \text{SiO}_2$ only 15 minutes); this apparently led to a homogeneous mixing of the oxides. Good statistical reproducibility was achieved with these annealed samples, provided the experimental temperature was kept above the melting point. The substrates were selected such that they were all liquids at 1300°C and solids at 1100°C (except $\text{Na}_2\text{O} \cdot \text{SiO}_2$).

Phase diagrams of the calcium iron silicate system (ref. 5,32) indicate phase separations at 1100°C , a fact verified also by microscopic examination. This was the most probable reason for the sometimes very erratic uptake at that temperature.

Preparation of the Radioactive Sources

The radioactive tracer solutions were evaporated to dryness of the bottom of the silica containers. In order to insure a layer as uniformly thin as possible, the following technique was adopted: the solutions were concentrated to a small volume, then absolute alcohol was added and evaporation continued to dryness. The drying continued overnight in order to insure removal of last traces of HCl , H_2O or alcohol.

A P P E N D I X B

Distribution of Activity

In each experiment measurements were made of the activity of each isotope in the melts, the quartz chamber, the source container (if other than the floor of the chamber), and the platinum loops. The diameter and weight of each melt were recorded, from which the density and surface areas were calculated.

The counting rate data were corrected for decay to a fiducial date and expressed as counts per minute per cm^2 or as counts per minute per mg. The cps per unit area data reflect the degree to which the quartz chamber and Pt surfaces compete for and retain the activity relative to the melts.

The Pt wire exposed an area of about 0.01 cm^2 per mg; the quartz surface was usually 78 cm^2 . The area of the substrate beads were individually about 0.2 cm^2 and collectively about 1.2 cm^2 (two types of melt, each in triplicate).

Typically, about 90% of the Mo was found in the melts, but a considerably smaller portion of the Cs. The attachment of Mo per unit area of quartz relative to the standard melt was about .001-.002. For Cs, on the other hand, attachment factors relative to the standard substrate were from 1.-1.0 in the various experiments.

Oxygen Ion Activity Calculations

The calculations of the results for ternary melts imply the knowledge and use of some parameter belonging to the binary silicates, two of which if mixed together would have the composition of a ternary melt. These silicates are listed in Table VII, and the compiled data there, as well as in Table VIII, were evaluated as described below.

Binary Silicates

The calculations are based on theoretical and experimental data as well as on mathematical expressions mentioned in the discussion.

In the case of alkali silicates, Charles' data for $\Delta G_{(\text{mix})}$ was used to estimate k through Eq. 20. Assuming a quantitative reaction to occur between the SiO_2 network and O^{2-} (from Na_2O) to form O^- , the free oxygen ion activity was calculated with Eq. (17).

For the CaO-SiO_2 and FeO-SiO_2 systems the just mentioned reaction is not quantitative¹³ and the results were obtained with Eq. (25) using thermodynamic data from the following sources: JANAF Tables²³, Rein and Chipman²⁴, Turkdogan²⁵, Kay and Taylor²⁶, Elliott²⁷, and Toop and Samis¹²; the (O^-) concentrations were calculated from Eq. (19).

The value for $2\text{AlO}_{1.5}\cdot\text{SiO}_2$, or Sillimanite, is based on Rein and Chipman's data²⁴ on mullite ($6\text{AlO}_{1.5}\cdot 2\text{SiO}_2$) at 1600°C : $\Delta G^\circ = 5.7$ kcal/mole, $\text{act.}(\text{SiO}_2) = 0.46$, $\text{act.}(\text{AlO}_{1.5}) \approx 1$. These were used in the well-known expression $\Delta G_{(\text{mix})} = RT(N_1 \ln a_1 + N_2 \ln a_2)$ yielding a value of 0.72 (see Table VII). The use of Eqs. (17), (18), (19), (21) leads to $k = 0.19$ which should also apply to sillimanite, whose (O^{2-}) activity was thus estimated as 0.54. Eq. (19)

had to be changed for this case to the form

$4(\text{O}^-)^2 k = [4 N_{\text{SiO}_2} - (\text{O}^-)] [3 - 2 N_{\text{SiO}_2} - 1.5 (\text{O}^-)]$ after taking into consideration the additional oxygen in aluminum oxide and applying this to some of Toop and Samis' equations. (This is due to the following reasoning: N_{SiO_2} moles of SiO_2 and $(1-N_{\text{SiO}_2})$ moles of O^{2-} should, in theory, combine to form silicate anions and free O^{2-} ions. But since the basic metal oxide dissociates only incompletely, the free O^{2-} per mole is

$$(\text{O}^{2-}) = (1.5 - N_{\text{SiO}_2}) - \frac{(\text{O}^-)}{2} = \frac{[3 - 2 N_{\text{SiO}_2} - 1.5 (\text{O}^-)]}{2}$$

while the double bonded oxygen is $(\text{O}^\circ) = \frac{4 N_{\text{SiO}_2} - (\text{O}^-)}{2}$ and

these two equations combined in Eq. (17) yield the above expression.)

The "ferric-silicate" data are based on Turkdogan's value of $\Delta G_{(\text{mix})} = 2.8$ kcal/mole (at 1550°)²⁵, which if introduced into Eq. (21)

gives the mole fraction of single bonded oxygens (O^-). This result and the use of Eqs. (17), (18), (19) lead to the double bonded (O^0), to k and finally to the (O^{2-}) -activity. This constant should of course apply to all the "ferric-silicate" melts, thus enabling the estimation of their individual activities. At 1600°C the ratio of ferric to total iron is only 0.71^{29} as compared to 0.95 at 1300°C^{31} , so Eq. (19) was changed accordingly to

$$4 (O^-) k = [4 N_{\text{SiO}_2} - (O^-)] [2.714 - 2 N_{\text{SiO}_2} - 1.357 (O^-)].$$

Ternary Melts

Theoretically, these melts could be synthesized from the binary silicates in Table VII by adding them up at various proportions. Logarithmic averages of the constants K and k as well as arithmetic averages of the singled bonded oxygens were taken and used to evaluate the oxygen ion activities according to the theoretical composition as shown in Table IX. For example, for the melt $\text{CaO} \cdot \text{FeO} \cdot 2 \text{SiO}_2$ (not investigated here) K was estimated by Eq. (24) as follows:

$$\ln \bar{K} = 0.5 \ln 0.03 + 0.5 \ln 0.39 = -3.382,$$

while k for melt VIII ($3 \text{CaO} \cdot 2 \text{AlO}_3 \cdot 7 \text{SiO}_2$) was obtained from:

$$\ln \bar{k} = 0.75 \ln 0.0017 + 0.25 \ln 0.19 = -5.198$$

The results for these ternary melts were calculated using Eq. (25) or Eqs. (17), (18), depending upon available data.

TABLE IX

THEORETICAL COMPOSITION OF TERNARY MELTS FOR PURPOSES OF CALCULATIONS

Melts from Literature	Synthesized theoretically from:
$\text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2$	$(2 \text{ CaO} \cdot \text{SiO}_2)_{1/2} + (2 \text{ FeO} \cdot \text{SiO}_2)_{1/2}$
$\text{CaO} \cdot \text{FeO} \cdot 2\text{SiO}_2$	$\text{CaO} \cdot \text{SiO}_2 + \text{FeO} \cdot \text{SiO}_2$
$\text{CaO} \cdot 2\text{FeO} \cdot \text{SiO}_2$	$(2 \text{ CaO} \cdot \text{SiO}_2)_{1/2} + (4 \text{ FeO} \cdot \text{SiO}_2)_{1/2}$
$3\text{CaO} \cdot 2\text{FeO} \cdot 7\text{SiO}_2$	$(\text{CaO} \cdot 2\text{SiO}_2)_3 + 2 \text{ FeO} \cdot \text{SiO}_2$
Melts Investigated	
I $\text{CaO} \cdot \text{FeO}_{1.5} \cdot \text{SiO}_2$	$(2 \text{ CaO} \cdot \text{SiO}_2)_{1/2} + (2\text{FeO}_{1.5} \cdot \text{SiO}_2)_{1/2}$
II $\text{CaO} \cdot \text{FeO}_{1.5} \cdot 2\text{SiO}_2$	$\text{CaO} \cdot \text{SiO}_2 + \text{FeO}_{1.5} \cdot \text{SiO}_2$
III $\text{CaO} \cdot 2\text{FeO}_{1.5} \cdot \text{SiO}_2$	$(2 \text{ CaO} \cdot \text{SiO}_2)_{1/2} + (4 \text{ FeO}_{1.5} \cdot \text{SiO}_2)_{1/2}$
VI $\text{Na}_2\text{O} \cdot 2\text{FeO}_{1.5} \cdot \text{SiO}_2$	$(2 \text{ Na}_2\text{O} \cdot \text{SiO}_2)_{1/2} + (4 \text{ FeO}_{1.5} \cdot \text{SiO}_2)_{1/2}$
IX $\text{CaO} \cdot \text{FeO}_{1.5} \cdot 7\text{AlO}_2$	$(\text{CaO} \cdot 2\text{SiO}_2)_3 + 2\text{FeO}_{1.5} \cdot \text{SiO}_2$
VIII $3\text{CaO} \cdot \text{AlO}_{1.5} \cdot 7\text{SiO}_2$	$(\text{CaO} \cdot 2\text{SiO}_2)_3 + 2 \text{ AlO}_{1.5} \cdot \text{SiO}_2$

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